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Authors
Wang, Xu-Chen
Druffel, Ellen R. M
Lee, Cindy

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Radiocarbon in organic compound classes in particulate organic matter and sediment in the deep northeast Pacific Ocean

Xu-Chen Wang and Ellen R. M. Druffel
Department of Earth System Science, University of California, Irvine

Cindy Lee
Marine Sciences Research Center, State University of New York, Stony Brook

Abstract. Radiocarbon ($\Delta^{14}C$) and stable carbon isotopes ($\delta^{13}C$) were measured for total amino acids, carbohydrates, lipids and acid-insoluble organic fractions separated from sinking particulate organic matter (POM$_{sink}$), detrital aggregates, sediment floe and sediments collected from the deep Northeast Pacific Ocean. The results show distinct $\Delta^{14}C$ signatures among these organic compound classes. Bomb $^{14}C$, produced 3-4 decades ago in the atmosphere, was present in all organic fractions in the POM$_{sink}$ in the deep sea. $\Delta^{14}C$ values decrease with depth, from the sediment trap POM$_{sink}$ (3450 m) to the sediment (4100 m), with rapid changes occurring at the sediment-water interface. Total lipid had much 'older' $\Delta^{14}C$ values than those of amino acid and carbohydrate fractions in detrital aggregates, sediment floe and sediments. These data demonstrate that two processes may be occurring: 1) preferential decomposition of organic matter at the sediment-water interface, and 2) incorporation of 'old' organic carbon into POM and sediment. The alteration of carbon found in these organic compound classes suggests that differences in decomposition and chemical behavior exist for each of these compound classes in the deep ocean.

Introduction

Lower amounts of bomb-produced radiocarbon ($^{14}C$) have been observed in deep-sea organisms (Pearcy and Stuiver, 1983; Williams et al., 1987) and particulate organic carbon suspended in deep sea water (Druffel and Williams, 1990; Druffel et al., 1992) compared to those in surface water. Adsorption of dissolved organic carbon (DOC) having low $^{14}C$-activity is a possible mechanism for lowering the $\Delta^{14}C$ signatures of bulk organic carbon pools in the deep-sea (Druffel and Williams, 1990; Druffel et al., 1996). Differential decomposition of the complex mixture of organic compounds in the ocean (Wakeham and Lee, 1993) could also cause lower $\Delta^{14}C$ values of bulk particulate organic carbon in the deep sea. Determination of $\Delta^{14}C$ and stable carbon isotope ($^{13}C/^{12}C$) ratios in the major organic compound classes can help establish sources of organic matter and thus differentiate between these two processes, DOC sorption and differential decomposition.

As part of a larger project to study radiocarbon of dissolved and particulate organic carbon cycling in the ocean, we investigated $^{14}C$ signatures of total lipid, total hydrolyzable amino acid (THAA), total carbohydrate (TCHO) and acid-insoluble fractions separated from POM$_{sink}$, detrital aggregates, sediment floe and sediments collected from the Northeast Pacific Ocean. In this paper, we report the first $\Delta^{14}C$ and $\delta^{13}C$ measurements of these major organic compound classes.

Materials and Methods

Samples were collected from a single site (Station M, 34°50'N, 123°00'W, 4100 m water depth) in the Northeast Pacific Ocean located 220 km west of Point Conception, California. Strong seasonal variability of primary production has been observed in the region (Michaelsen et al., 1988). Station M has been occupied several times per year since 1987 for a time-series study of the relationship between deep carbon fluxes and benthic boundary layer communities (Smith et al., 1994).

POM$_{sink}$ samples were collected using a Teflon-coated, double fibreglass-cone time-series sediment trap (120 cm long, 57 cm diameter) moored at 695 mab (meters above bottom, 3450 m depth) as described by Smith et al. (1994). Mercuric chloride was used as a poison. Two samples taken from the trap were collected during 1-10 June (cup #11) and 21-30 June (cup #13), 1993. POM$_{sink}$ was concentrated by gentle vacuum filtration of trap liquid onto a 45-mm pre-combusted, quartz-fiber filter (0.8 µm) and frozen immediately (Druffel et al. 1996). A sediment core was collected using a free-vehicle grab respirometer (Smith et al., 1994) in July, 1993. The core was sectioned at 0.5 cm intervals on board and frozen immediately in glass jars at -20°C. Cores were also collected using plastic core liners (7 cm o.d.) during DSV Alvin dives in September, 1994. Detrital aggregates (clumps of amorphous brown particulate matter typically with ellipsoid shapes ranging from 0.6-191 cm$^2$ (Smith et al., 1994)) and a sediment floc sample (top 2-4 mm of flocculent layer of sediment) were collected from the sediment surface of these cores. Detrital aggregates were removed from the top of the core using a 25-ml plastic pipette and frozen immediately in glass. Sediment floc was then taken using the same pipette and frozen immediately in glass. All tools and glassware were pre-combusted at 550°C. These POM$_{floc}$, sediment, detrital aggregate and sediment floc samples were collected on two cruises, both during high flux periods (Smith et al., 1994).

Samples were first oven-dried at 50°C and then separated into THAA, TCHO, lipid and acid-insoluble fractions. As little as a few milligrams organic carbon for each sample type were separated into component organic classes. Methods used to separate these organic compound classes are described in detail in X-C. Wang et al. (submitted to Geochim. Cosmochim. Acta, 1996). In brief, dried samples were first extracted for total lipids with high purity methylene chloride:methanol (2:1, v/v). After lipid extraction, samples were dried and divided into two fractions for THAA and TCHO extraction. The THAA fraction was hydrolyzed with 6N Ultrapure HCl under N$_2$ at 100°C for 19 h and free amino acids isolated by cation exchange chromatography. Insoluble material after hydrolysis
was defined as the HCl-insoluble fraction. The TCHO fraction was hydrolyzed with 1.2 M H2SO4 at 100°C for 3 h and free sugars isolated by cation/anion column chromatography (Cowie and Hedges, 1984). The recovery efficiency of the method for each organic fraction tested using standard compounds were 90% for amino acids, 97% for sugars and 98% for lipids, respectively (X-C. Wang et al., submitted to GCA, 1996).

Samples of each organic fraction and bulk organic carbon (TOC) were acidified and combusted to CO2 in sealed quartz tubes at 850°C for 1-2 h according to standard techniques (Druffel et al., 1992). CO2 was then split into two aliquots for 14C and 13C analyses. The CO2 for 14C measurement was converted to graphite (Vogel et al., 1987) and 14C was measured using accelerator mass spectrometry (AMS) at Lawrence Livermore National Laboratories (LLNL) AMS Research Center. Radiocarbon values are reported as Δ14C (per mil deviation from the 'standard' activity of 19th century wood) (Stuiver and Polach, 1977). Blanks were also conducted for each organic fraction extraction and the blank CO2 produced during sample processing steps of each organic fraction extraction and blank carbon produced during graphitization. δ13C was measured on every sample with an overall error of ± 0.10‰ and all values are corrected for blanks. TOC% was measured using a Carlo Erba 200 CHN analyzer with an overall error of ± 8% of the mean.

Results and Discussion

Mass balance calculations showed that the total recovery of carbon when each organic fraction was summed accounted for 82-108% of the total organic carbon (TOC) measured in the samples (Table 1). Δ14C balance summing the contribution of Δ14C in each organic fraction also showed good agreement with TOC (Table 1), suggesting that contamination during sample processing was small. The THAA fraction accounted for an average of 26% of the TOC in POMsink, 19% in the detrital aggregates, 27% in sediment floc and 17% in the sediment. Carbon abundances of the TCHO fraction were only slightly lower in all samples (See Table 1) than those in THAA. Total lipid carbon accounted for 13% of TOC in POMsink, but only 5-8%, 4% and 3% in detrital aggregates, sediment floc and sediment, respectively.

Δ14C values of bulk TOC and the four organic fractions in POMsink ranged from -56‰ to +57‰, clearly showing the presence of post-bomb, surface-derived carbon in the deep POMsink pool at 650 mab (Fig. 1), compared with pre-bomb Δ14C values of ~70‰ (Berger et al., 1966) for surface water in this region. Detrital aggregate Δ14C values were intermediate (except one sugar sample) between POMsink (high) and sediment floc (low) values, suggesting that the detrital aggregates have a smaller

![Figure 1. Δ14C of a) THAA, b) TCHO, c) lipids and d) acid-insoluble fractions and e) TOC separated from POMsink detrital aggregates, sediment floc and sediment as a function of depth at Station M in the Northeast Pacific Ocean. Water depth at Station M is 4100 m. Water column depth is plotted as meters above bottom (mab). A horizontal line indicates the sediment-water interface. Average Δ14C values of the duplicate measurements of the five selected samples were plotted. 2σ error bar is indicated on figure.](image-url)
amount of ‘old’ or deep ocean carbon than does the sediment floc. $\Delta^{14}C$ of TOC and the organic fractions decreased further with depth in the sediment with values generally ranging from $-92\%o$ (0-1 cm, TCHO) to $-472\%o$ (4-5 cm, lipids). In general, THAA and TCHO fractions had similar $\Delta^{14}C$ values that were higher than those of total lipid and acid-insoluble fractions in all samples.

$\delta^{13}C$ values of bulk TOC and THAA, TCHO, lipid and acid-insoluble fractions are generally consistent with a marine phytoplankton source (Fig. 2). THAA and TCHO had similar $\delta^{13}C$ values, ranging from $-16.7\%o$ to $-19.5\%o$, indicating that these compound classes are derived from marine organic matter (Epstein, 1977; Monson and Hayes, 1982). The $\delta^{13}C$ values in organic fractions show less variation at the sediment-water interface and in the sediment suggesting that their $\delta^{13}C$ signature is unaffected by organic decomposition processes.

The decrease of $\Delta^{14}C$ in individual organic compound classes between POM$_{444}$ from 650mab and the surface sediment indicates that several possible processes are occurring: 1) bioturbation and sediment resuspension which dilutes the surface $\Delta^{14}C$ with ‘old’ carbon from deeper sediment; 2) rapid organic matter decomposition at the sediment-water interface during which most surface-derived, labile organic matter is remineralized (e.g., Mayer, 1993); 3) incorporation of ‘old’ organic matter at depth in the water column by either sorption or bacterial utilization of ‘old’ DOC ($\Delta^{14}C$ of DOC = $-540\%o$ at depths of 1600-4050m at Station M, J. Bauer et al., submitted to J. Geophys. Res., 1996) and subsequent incorporation into POC; and 4) chemoeutrophic and anaplerotic reactions (Lehninger, 1970) by organisms in the water column that use deep, ‘old’ dissolved inorganic carbon (DIC) to produce POC (Rau, 1991). Advection transport of suspended ‘old’ carbon from continental shelf sediments to Station M could also dilute $\Delta^{14}C$ signatures at the sediment surface. However, $\Delta^{14}C$ measurements of suspended particulate organic carbon collected in the deep water at Station M indicate that this lateral transport effect is likely small (Druffel et al., 1996).

If remineralization were the only process affecting the average $\Delta^{14}C$ signal of POM$_{444}$, then at least some surface organic matter would have had a $\Delta^{14}C$ signature of +243$. This is calculated from $\Delta^{14}C$ values of +15%o for POM$_{444}$ and -180%o for detrital aggregates (Fig. 1). Since the decrease in organic C content from POM$_{444}$ (3.7%) to detrital aggregates (2.0%) indicates a 46% loss in carbon, the C in POM$_{444}$ that is remineralized by the time it reaches the sediment surface must have had a $\Delta^{14}C$ of +243%o [$ (243\%o \times 0.46) + (-180\%o \times 0.54) = 15\%o$] to result in detrital aggregates with $\Delta^{14}C$ of -180%o. However, the highest possible $\Delta^{14}C$ value of organic matter that can be produced in the euphotic zone at Station M was used to calculate the $\Delta^{14}C$ depletion of detrital aggregates. DOC (including colloidal organic C) could be sorbed by particles or incorporated by bacteria associated with POM (Cho and Azam, 1988; Lochte and Turley, 1988). More hydrophobic compounds such as lipids may be sorbed more strongly which would result in an even lower $\Delta^{14}C$ signature for the lipid fraction, as seen in Fig. 1c. If the sorption of deep DOC were responsible for lowering the $\Delta^{14}C$ of POC$_{444}$ from +15%o to a value of $-180\%o$ as measured in the detrital aggregates, then approximately 35% of the C in detrital aggregates would have to be contributed from deep DOC. A similar calculation for each organic fraction indicates that 18%, 27%, 37% and 48% of the C in THAA, TCHO, lipid and acid-insoluble fractions, respectively, in the detrital aggregates would have to be contributed from deep DOC. More ‘old’ C incorporated into the lipid and acid-insoluble fractions than in the THAA and TCHO fractions supports the DOC sorption explanation above.

Bioturbation that resulted in upward transport and mixing of deeper, older sediment likely resulted in older $\Delta^{14}C$ values in surface sediment and to a lesser degree in detrital aggregates. The decreasing values of $\Delta^{14}C$ with depth in the water column and sediment likely reflect in part, a mixing curve whose end members are young surface organisms and old deep sediment. The differences in mixing processes at various sites, e.g., the sediment-water interface, would explain observed irregularities in the mixing line. Although the decrease in $\Delta^{14}C$ values with depth that was observed in suspended POM at Station M was attributed to sorption of ‘old’ DOC (Druffel...
et al., 1996), some of the decrease of $\Delta^{14}C$ observed at the sediment-water interface may be due to mixing with older particles from the benthic boundary layer.

Selective decomposition is a more likely cause of the large differences between $\Delta^{14}C$ of lipids and THAA/TCHO fractions at Station M. Selective remineralization of labile lipids (e.g. fatty acids) over more refractory alkanes (e.g. long chain hydrocarbon) has been determined in sediment trap POM (Wakeham et al., 1984; Wakeham and Caneel, 1988). If the alkanes have lower $\Delta^{14}C$ values (from age in the water column and/or fossil origin), this would explain part of the large gradient of $\Delta^{14}C$ in total lipids (300% to 500%) between POM and sediments. It is also possible that consumption of "old" DOC by bacteria at depth and conversion to bacterial membrane lipids could contribute to the lipid pool, and hence have an older $^{14}C$ signature (T. Eglinton, personal communication). To distinguish these causes, further $\Delta^{14}C$ measurements and lipid determination at the molecular level will help to identify the important processes (Eglinton et al., 1996). Some "old" THAA and TCHO may be produced by microbes from old carbon at the sediment-water interface, thus diluting the modern $^{14}C$ from surface-derived carbon.

In summary, the results from this study suggest that radiocarbon measurements at the organic compound class level can provide advanced information for organic geochemical studies in the ocean. Preferential decomposition of organic matter and sorption/incorporation of "old" DOC onto POM may be important processes that affect the distribution and geochemical behavior of total lipid, THAA and TCHO in POM and sediment of the Northeast Pacific Ocean. Carbon alteration among different organic fractions in the deep Northeast Pacific may indicate different carbon origins and decomposition pathways. Further studies, including determination of temporal and spatial $\Delta^{14}C$ distributions in sinking POM and $\Delta^{14}C$ analysis at the molecular level are needed to solve these important issues.

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References


